O 96: Focus Session: Molecular Nanostructures on surfaces - New Concepts towards Complex Architectures VI

Organizers: Sabine Maier, FAU Erlangen-Nürnberg; Meike Stöhr, University of Groningen

(Synopsis provided with part I of this session)

Time: Thursday 15:00–18:15 Location: MA 004

O 96.1 Thu 15:00 MA 004

On-Surface Synthesis and Characterization of an Iron Corrole — •Martin Schmid[1], Malte Zugermeier[1], Jan Herritsch[1], Benedikt Klein[1], Claudio Krug[1], Lukas Ruppenthal[1], Philipp Müller[1], Martin Bröring[2], and J. Michael Gottfried[1] — [1]Philipps-Universität Marburg, Fachbereich Chemie, Marburg, Germany — [2]Technische Universität Braunschweig, Institut für Anorganische und Analytische Chemie, Braunschweig, Germany

Tetrapyrrole layers (e.g. porphyrins or phthalocyanines) can be metalated with an on-surface reaction scheme under UHV conditions to obtain the corresponding metallo-tetrapyrroles, in which the metal atoms usually have a +II oxidation state. In order to obtain different oxidation states in the tetrapyrrole films, we examined an alternative class of molecules: corroles. Corroles differ from porphyrins by the absence of one bridging CH unit between two pyrrole units and the presence of a further hydrogen atom in the central pocket of the molecule. Thus, one could expect to find metal atoms in a +III oxidation state. We prepared multilayers and monolayers of 3H-hexaethyl-dimethyl-corrole (3H-HEDMC) on Ag(111) and performed a series of in-situ metalation experiments wit Fe. We analyzed the systems with XPS, UPS, NEXAFS and STM. We find that the corrole ligands can be in-situ metalated and that the iron metal centers are in a +III oxidation state in the multilayer. Additional comparative measurements with Fe(II)-octaethylporphyrin monolayers elucidate differences in the valence electronic structure between Fe(II) and Fe(III) tetrapyrroles on Ag(111).

O 96.2 Thu 15:15 MA 004

On-surface Metalation of the Salophene Ligand and Investigations of local Electronic Properties — •Micha Elsebach[1], Julia Goedecke[1], Emil Sierda[1,2], Marta Przychodnia[2], Maciej Bazarnik[1,2], and Roland Wiesendanger[1] — [1]Dept. of Physics, University of Hamburg, D-20355 Hamburg, Germany — [2]Institute of Physics, Poznan University of Technology, Piotrowo 3, 60-965 Poznan, Poland

Due to their electronic and magnetic properties in combination with their versatility, molecular systems promise high potential for future application in spintronic devices. Previously we showed that Co-salophenes can be used for the fabrication of an all-spin-based logic gate on Au(111) [1]. However, the Co-atoms within the salophene ligand are in the second oxidation state and therefore carry only spin $\frac{1}{2}$. Other metal centers will have a different spin state and therefore might present stronger magnetic coupling within a chain of molecules created by the Ullmann coupling.

The chemical synthesis of complexes based on the salophene ligand in solution is a difficult task that bears the problem of getting a clean sample of the desired complex. Therefore, we performed on-surface metalation of an empty salophene ligand terminated with two H-atoms. During this procedure the creation of counter ions and other secondary products is highly improbable. Here, we present STM and STS studies on the on-surface metalated molecules, and their *ex situ* synthesized counterparts.

[1] M. Bazarnik et al., Nano Lett. 16, 577 (2016).

O 96.3 Thu 15:30 MA 004

On-surface synthesis of Si-porphyrins — •Aleksandr Baklanov, Manuela Garnica, Knud Seufert, and Willi Auwärter — Physik Department E20, Technische Universität München, James Franck Str. 1, 85748 Garching, Germany

On-surface synthesis of non-metal porphyrins is insufficiently explored, although it could open up a possibility to investigate new complexes. Specifically, silicon porphyrins have attracted attention due to their interesting structure and properties [1]. Here we report silicon functionalized tetraphenylporphyrin (Si-TPP) molecules synthesized on a Ag(100) single crystal surface at room temperature in UHV conditions. Self-assembly and electronic properties of Si-TPP were probed by scanning tunneling microscopy/spectroscopy (STM/STS) and X-ray photoelectron (XP) spectroscopy. The N1s XP spectrum of 2H-TPP contains two peaks corresponding to imminic and pyrrolic nitrogen species, whereas in the Si-TPP case only one peak is observed, indicating that all four nitrogen atoms in the macrocycle are chemically identical. A similar behavior is typical for metalloporphyrins [2]. The C1s signal is not affected by the incorporation of Si in the macrocycle. In STM, Si-TPP can be clearly distinguished from 2H-TPP species by additional protrusions at negative sample bias voltages. Furthermore, STS indicates a change of the 2H-TPP LUMO with the Si-complexation.

[1] J. A. Cissell et al., J. Am. Chem. Soc. **127**, 12212 (2005).

[2] A. C. Papageorgiou et al., J. Phys. Chem. C **120**, 8751 (2016).

O 96.4 Thu 15:45 MA 004

On the Adsorption Behavior of Cyano-Functionalized Porphyrins on Cu(111) and Ag(111): from Dimers over Molecular Wires to Ordered Supramolecular Two-Dimensional Aggregates — Michael Lepper[1], Gretel Siglreithmaier[1], Martin Gurrath[2], Bernd Meyer[2], Hans-Peter Steinrück[1], and •Hubertus Marbach[1] — [1]Lehrstuhl für Physikalische Chemie II — [2]Computer-Chemistry-Center; both Universität Erlangen-Nürnberg

We investigate the impact of peripheral cyano functionalization of the well-studied 2H-tetraphenylporphyrin (2HTPP) by scanning tunneling microscopy (STM) and density functional theory (DFT). Interestingly, depending on the number and the geometry of cyano-functionalized phenyl rings, the free-base porphyrins form dimers or 1D-cains after mild annealing on Cu(111). The linking within the dimers and chains is realized by Cu adatoms as evidenced by comparison of STM and DFT [1]. In contrast, the corresponding Cu-porphyrin analogues form peculiar porous highly ordered 2D-islands on Cu(111). On Ag(111), the cyano-functionalized free-base porphyrin molecules assemble into a long-range 2D square order similar to their analogues without cyano functionalization [1]. We will discuss the presented results in regard of the specific roles of molecule-molecule and molecule-substrate interactions, with a particular emphasis on the specific intramolecular conformations [2] and the potential to tailor-make functional molecular architectures. [1] M. Lepper et al., J. Phys. Chem. C, (2017) DOI: 10.1039/C7CC04182A [2] F. Albrecht et al., NanoLett. 16 (2016) 7703; M. Lepper et al., Chemical Communications, 53 (2017) 8207

O 96.5 Thu 16:00 MA 004

Site-Dependent Conformation of Fe-phthalocyanine on Fe/W(001) — •Alexander Schwarz, Josef Grenz, and Roland Wiesendanger — INF, University of Hamburg, Jungiusstr. 11, 20355 Hamburg

Molecules possess many degrees of freedom and are thus able to adsorb on the same surface on different sites, in different orientation and conformations. Here, we present submolecular resolution results obtained with atomic force microscopy in the non-contact mode of operation at low temperatures on well separated Fe-phtalocyanine molecules deposited onto the Fe monolayer on W(001).

The molecules adsorbs with its central Fe atom on hollow-, bridge- and top-sites in different orientations relative to the substrate. Only on hollow sites the molecule appears planar with a fourfold C_4 symmetry and a central protrusion. On the other two adsorptions sites the central region always exhibits a depression and the outer isoindole ligands appear distorted, which results in a reduced symmetry. We will discuss the origin of the distortion and the role of the bonding between the substrate and the central Fe atom of the molecule as well as the importance of the interaction between the nitrogen atoms in the macrocycle and the substrate.

O 96.6 Thu 16:15 MA 004

Digging for silver – surface chemistry of tin(IV)-phthalocyanine-dichloride on Ag(111) — •C. Zwick[1], E. Wruss[2], G. van Straaten[3], M. Gruenewald[1], T. Ueba[4], R. Forker[1], C. Kumpf[3], S. Kera[4,5], E. Zojer[2], and T. Fritz[1] — [1]FSU Jena, Germany — [2]TU Graz, Austria — [3]Forschungszentrum Jülich, Germany — [4]IMS Okazaki, Japan — [5]Chiba University, Japan

The peculiarities of the dye molecule tin(IV)-phthalocyanine-dichloride ($SnCl_2Pc$) originate from its functionalization with Cl atoms above and below the central tin atom. These are expected to crucially impact on interface formation due to the altered chemical reactivity compared to Cl-free phthalocyanines. We report on the monolayer growth of $SnCl_2Pc$ on Ag(111), focusing on the role played by the Cl atoms in terms of structure formation and surface chemistry. By combining state-of-the-art low-temperature scanning probe microscopy (SPM), distortion-corrected low-energy electron diffraction (LEED) and X-ray standing waves (XSW) measurements, an extensive structural characterization could be realized. This includes the lateral and vertical adsorption geometry of the molecules within the adlayer as well as its epitaxial relation to the substrate. Evidence of chemically altered molecules due to a surface reaction was found by means of SPM and photoelectron emission spectroscopy (PES). Simulations based on density functional theory (DFT) support this conclusion. In this regard, one of the most crucial aspects is the partial dechlorination of $SnCl_2Pc$ to SnClPc. Surprisingly, the single remaining Cl atom is penetrating the silver surface, substituting Ag atoms.

15 min. break

O 96.7 Thu 16:45 MA 004

Structural transformation of surface-confined porphyrin networks via addition of Co atoms — •Brian Baker[1], Florian Studener[1], Kathrin Müller[1], Mihaela Enache[1], Nicolas Marets[2], Veronique Bulach[2], Mir Wais Hosseini[2], and Meike Stöhr[1] — [1]Zernike Institute for Advanced Materials, University of Groningen — [2]Laboratoire de Tectonique Moleculaire, UMR UDS-CNRS 7140, Universite de Strasbourg

The self-assembly process of a nickel-porphyrin (Ni-DPPyP) derivative containing two pyridyl coordinating sites and two pentyl chains at trans meso positions under ultrahigh vacuum on Au(111) was studied with scanning tunneling microscopy (STM), X-ray photoelectron spectroscopy (XPS) and low energy electron diffraction (LEED). Deposition of Ni-DPPyP onto Au(111) gave rise to the formation of a close-packed network with a square unit cell as revealed by STM and LEED. The molecular arrangement of this two-dimensional network is stabilized via hydrogen bonds formed between the pyridyl's nitrogen and hydrogen atoms from the pyrrole groups of neighboring molecules. Subsequent deposition of cobalt atoms onto the close-packed network and annealing at 150 degrees celsius lead to the formation of a Co-coordinated hexagonal porous network with a rhombic unit cell. The Co-coordinated network is stabilized by metal-ligand bonds between one cobalt atom and three pyridyl ligands, each pyridyl ligand coming from a different Ni-DPPyP molecule.

O 96.8 Thu 17:00 MA 004

Molecular adsorption of 5, 15-diphenylporphyrin on CoO (111) films — •Feifei Xiang and M. Alexander Schneider — Solid State Physics, Friedrich-Alexander-University Erlangen-Nürnberg (FAU), Erlangen, Germany

The adsorption geometry of 5, 15-diphenylporphyrin (2H-DPP) on a ~2.7 nm thick CoO (111) film is studied by low temperature scanning tunneling microscopy. Although CoO is a semiconductor, the oxygen terminated CoO (111) film shows metallic properties according to scanning tunneling spectroscopy data.[1] When deposited at 170 K, 2H-DPP adsorbs as single, flat-lying molecules on the surface due to the hydrogen bonding between the molecule and the surface.[2] With annealing of the molecular adsorbate system, 2H-DPP starts to have reactions with the oxide surface, causing the characteristic changes of its configuration from the original oval shape to a bean shape and eventually to a symmetric feature with reduced apparent molecular width at 470K. From comparison with Co-DPP deposited on CoO (111), we conclude that 2H-DPP gets metalated at around room temperature.

[1] Meyer, W., et al. Phys. Rev. Lett., 2008, 101, 016103.
[2] Wang, C., Chem. Commun., 2014, 50, 8291-8294.

O 96.9 Thu 17:15 MA 004

Porphyrins at surfaces: effect of film formation on the electronic levels — Osman Baris Malcioglu and •Michel Bockstedte — Chemistry and Physics of Materials, University of Salzburg, Salzburg, Austria

Porphyrins on surfaces are used successfully in various applications such as surface catalysis, lighting and energy harvesting. In order to unravel electronic and photophysical properties of such porphyrin films on surfaces, one first has to identify the contribution of the film's supramolecular network. Here, we investigate quasiparticle spectrum of amorphous and crystalline porphyrin structure as a model for supramolecular films of H2TPP and MgTPP. We use VdW-DFT and sc-GW approaches (calibrated against NIST data). We show that the crystalline model agrees with the UPS/2PPE spectra [1] better than individual molecules or other porphyrin structures regarding the position of the HOMO and LUMO state. The interaction of the phenyl rings has strong influence one the position and dispersion of quasiparticle levels of the prophyrin film. Our findings confirm that the systematic control of the film crystallisation or the substitution of residues enables an improvement or tuning of the electronic states and thus leads to better performance of devices [3].

[1] A. Classen, et al., Phys. Rev. B **95**, 115414 (2017).
[2] M. Gamboa, M. Campos, and L.A. Torres, J. Chem. Thermodynamics **42**, 666 (2010)
[3] A. Charisiadis *et al.*, ChemPlusChem, **82**, (2017).

O 96.10 Thu 17:30 MA 004

Charge state control of F_{16}CoPc on *h*-BN/Cu(111) — •Mathias Pörtner[1], Yinying Wei[2], Alexander Riss[1], Knud Seufert[1], Manuela Garcia[1], Johannes V. Barth[1], Lars Diekhöner[2], and Willi Auwärter[1] — [1]Physik-Department E20, Technische Universität München, James-Franck-Str. 1, D-85748 Garching, Germany — [2]Department of Physics and Nanotechnology, Fredrik Bajers Vej 5, DK-9100 Aalborg, Denmark

Molecules on metal supported hexagonal boron nitride (*h*-BN) are of great interest as far as their electronic properties and self-assemblies are accessible by scanning probe methods [1]. Here, we report on the control of the charge state of F_{16}CoPc on atomically thin *h*-BN on Cu(111) studied by low temperature scanning tunneling microscopy and spectroscopy. In the submonolayer regime, molecules adsorb on pore areas of the work-function template *h*-BN/Cu(111) [2]. Tunneling spectroscopy shows that the charge state of F_{16}CoPc can be controlled by three parameters: (i) template-induced gating by the work-function variation of *h*-BN/Cu(111) [2], (ii) field-induced gating by the STM tip [3] and (iii) screening, which depends on the neighboring molecules [4]. These parameters influence the properties of the molecular layer and thus its (templating) functionality. For example the preferred adsorption positions of second layer molecules differ from the first layer.

[1] Kumar, et al., Nanotechnology **28**, 082001 (2017).
[2] Joshi, et al., ACS Nano **8**, 430 (2014).
[3] Liu, et al., ASC Nano **9**, 10125 (2015).
[4] Cochrane, et al., Nat. Commun. **6**, 8312 (2015).

O 96.11 Thu 17:45 MA 004

Apparent reversal of molecular orbitals reveals entanglement — Ping Yu[1,2], Nemania Kocic[1], Benjamin Siegert[3], Jascha Repp[1], and •Andrea Donarini[3] — [1]Institute of Experimental and Applied Physics, University of Regensburg, 93053 Regensburg, Germany — [2]School of Physical Science and Technology, ShanghaiTech University, 201210 Shanghai, China — [3]Institute of Theoretical Physics, University of Regensburg, 93053 Regensburg, Germany

The frontier orbital sequence of individual dicyanovinyl-substituted oligothiophene molecules is studied by means of scanning tunneling microscopy. On NaCl/Cu(111) the molecules are neutral, and the two lowest unoccupied molecular states are observed in the expected order of increasing energy. On NaCl/Cu(311), where the molecules are negatively charged, the sequence of two observed molecular orbitals is reversed, such that the one with one more nodal plane appears lower in energy. These experimental results, in open contradiction with a single-particle interpretation, are explained by a many-body theory predicting a strongly entangled doubly charged ground state.

O 96.12 Thu 18:00 MA 004

Magnetism of Salophene based molecules — •Emil Sierda[1,2], Micha Elsebach[1], Maciej Bazarnik[1,2], and Roland Wiesendanger[1] — [1]Department of Physics, University of Hamburg, Jungiusstrasse 11, D-20355, Hamburg, Germany — [2]Institute of Physics, Poznan University of Technology, Piotrowo 3, 60-965, Poznan, Poland

Advances in molecular spintronics rely on the in-depth characterization of the molecular building blocks in terms of their electronic and magnetic properties. For this purpose inert substrates are required that will interact only weakly with adsorbed molecules in order to preserve their electronic states. Magnetic substrates, on the other hand, are useful for stabilizing the magnetic moment of a molecule, thereby making it accessible for investigations by spin-polarized scanning tunneling microscopy (SP-STM) [1].

Here, we present a SP-STM study of Salophene-based molecules with different transition metal centers adsorbed on Co-intercalated graphene on Ir(111) [2]. This substrate is an ideal choice for a thorough characterization of the molecules* electronic and magnetic states. In particular, such studies reveal the differences in magnetic structure between molecules with different transition metal centers. Based on these insights the most promising molecules in view of future molecular spintronic devices can be identified.

[1] Schwöbel, J. et al. Nat. Comm. 3, 953 (2012). [2] Decker R. et al. Phys. Rev. B 87, 041403 (2013).